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Scott Environmental Technology, Inc.
Plumsteadville, PA

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FIELD VALIDATION OF EPA REFERENCE METHOD 23

by

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Contract No. 68-02-3405

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The accuracy and precision of U.S. Environmental Protection Agency Reference Method 23 was evaluated at a trichloroethylene degreasing facility and an ethylene dichloride plant. The method consists of a procedure for obtaining an integrated sample followed by gas chromatographic analysis. Thie study identified a number of conditions such as sunlight and sample volume that may affect the performance of the Mehtod. A paired sampling technique was employed to obtain identical samples, from which the precision and variable interactions could be determined. Certain results fell outside the range of acceptable precision, especially when mylar bags were employed. Modifications to the method are suggested that specify that only Tedlar bags be used for sampling, that incorporate an on-site technique for leak detection, and that discontinues the procedure for moisture removal. With these modifications, Reference Method 23 was fully validated as acceptable for field use.

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FOREWORD

Measurement and monitoring research efforts are designed to anticipate potential environmental problems, to support regulatory actions by developing an in-depth understanding of the nature and processes that impact health and the ecology, to provide innovative means of monitoring compliance with regulations, and to evaluate the effectiveness of health and environmental protection efforts through the monitoring of long-term trends. The Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina, has responsibility for: assessment of environmental monitoring technology and systems; implementation of agency-wide quality assurance programs for air pollution measurement systems; and supplying technical support to other groups in the Agency, including the Office of Air, Noise and Radiation, the Office of Toxic Substances, and the Office of Enforcement.

This investigation was conducted at the request of the Office of Air Quality Planning and Standards. A test method for the measurement of halogenated hydrocarbon emissions from stationary sources, EPA Reference Method 23, was validated. Previously, we have reported laboratory studies that led to the development of this Method. In the present study, the Method was tested at a trichloroethylene degreasing facility and an ethylene dichloride manufacturing plant. Paired sampling techniques were used to determine the sensitivity of the Method to the variation of several analytical parameters and to measure its precision.

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ABSTRACT

The accuracy and precision of U.S. Environmental Protection Agency Reference Method 23 for use in the field was evaluated at a trichloroethylene degreasing facility and an ethylene dichloride manufacturing facility. The method consists of a procedure for obtaining an integrated sample followed by gas chromatographic analysis. This study identified a number of conditions such as sunlight and sample volume that may affect the performance of the Method in the field. Results obtained in the presence and absence of these conditions were compared. The most significant variable was the use of Tedlar (E. I. Dupont de Nemours & Company, Inc.) versus mylar bags as sampling containers, a choice left open in the method as originally defined.

A paired sampling technique was employed to obtain identical chemical samples from two sampling trains operating simultaneously. Certain results fell outside the range of acceptable precision, due to the use of mylar bags and to rigid sample containers that were prone to leakage. The method was modified to specify that only Tedlar bags be used for sampling; to incorporate an on-site technique for early leak detection; and to discontinue procedures for moisture removal. With these modifications, U.S. Environmental Protection Agency Reference Method 23 was fully validated as acceptable for field use.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
Acknowledgement. viii

1. Introduction 1
2. Conclusions and Recommendations 3
3. Experimental 4
4. Results and Discussion 14

References 18
Appendices

A. Field Data Summary 19

B. Field Audit Report 22

C. Method for the Determination of Halogenated Organics from Stationary Sources 26

FIGURES

Number		Page
1	Sampling train on atmospheric vent	3
2	Sampling train on pressurized vent	6
3	Leak-check apparatus	7
4	Allowable leakage rate per sampling rate, EDC, TCE. Calculated values for a 30-gallon rigid container using an orifice flow equation	8
5	Gas chromatograph column configuration with backflush	11
6	Adsorption profile of silica gel with EDC, TCE, and CCl_4	16

TABLES

Number		Page
1	Method 23 Evaluation Test Variables, Train B, TCE and EDC	9
2	TCE field evaluation results	14
3	EDC field evaluation results	15
4	Sample degradation over time	17

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SECTION 1

INTRODUCTION

On June 11, 1980, under Section 111 of the Clean Air Act, the U.S. Environmental Protection Agency (EPA) proposed standards limiting the emissions of chlorinated hydrocarbons from solvent degreasers, after determining that these substances presented a potential danger to public health and welfare. A national emission standard was proposed to include a method for measuring chlorinated hydrocarbons that was designated EPA Reference Method 23. The Quality Assurance Division of the Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina, has a program to evaluate and standardize EPA source test methods. While participating in this program, Scott Environmental Technology, Inc., undertook an investigation of Method 23, which is the subject of the present study.

Field evaluations of Method 23 were conducted at a metal degreasing facility using trichlorethylene (TCE) and at an ethylene dichloride (EDC) plant. The evaluations were part of the research performed by Scott Environmental Technology, Inc. under EPA Contract No. 68-02-3405, Directive Nos. 11 and 12.

Reference Method 23 for the Determination of Halogenated Organics from Stationary Sources consists of an integrated sampling procedure followed by gas chromatographic (GC) analysis.[1,2] The evaluation was designed to determine the effect of a number of variables that may exist under typical field conditions. The effect of these variables was demonstrated by a modification of Youden's ruggedness test,[3] in which a paired sampling technique is used to obtain duplicate samples by operating two or more sampling trains simultaneously. This assures that sample differences occur only as a result of variations in sampling and analytical conditions.

The goal in this evaluation was to test the accuracy of the Reference Method 23 apparatus and procedures by varying the field conditions of sunlight, sample volume, storage temperature, and storage time before analysis. Perhaps the most significant variable tested concerned the use of polyvinyl bags as sampling containers. The option of using either Tedlar or aluminized mylar bags was left open in the Reference Method as originally written. At the high concentrations encountered in source sampling, major problems can result from sample contamination due to prior use of the bags. Although in the past experience of this laboratory, Tedlar bags have been able to preserve sample concentrations better than mylar, for this evaluation program we wished to establish definitive results.

A potential difficulty with Tedlar bags was indicated by the review

of Seila et al.[4] The bags have the capacity to retain "memory traces" of EDC, which, under conditions of simulated sunlight, result in contamination peaks. Avoiding the problem would require the use of new bags for each experiment. More positive results were reported recently for Tedlar bags, as regard our research needs. Tedlar bags were successfully employed for source samples of vinyl chloride[5], benzene[6,7], and, under laboratory conditions, for a number of halogenated hydrocarbon gas mixtures.[1,2]

Paired sampling trains were used to test the utility of Tedlar and mylar bags for preserving field samples and to test the effects of the variables mentioned above. Results obtained under strict adherence to Method 23 were compared to the results obtained from varying these parameters, using both kinds of bags. Audit standards were used to verify the concentration figures. In addition to validation of Method 23, the most significant outcome of the investigation regarded the reliability of Tedlar bags.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

Field evaluations at TCE and EDC sources showed Tedlar bags to be considerably more reliable sample containers than mylar bags. The use of mylar bags consistently yielded results which were as much as 43% lower than concentrations measured with Tedlar bags. We recommend the use of Tedlar bags only as sampling containers for Method 23.

Leakage was identified as a significant source of error for rigid sample containers, probes, and bag connections. It became a particular problem at low sampling rates. For early detection of leaks, field procedures that adequately corrected the situation were developed and are recommended for future use in Method 23. All sample runs employing this procedure produced full bags at the end of the tests.

High moisture content was determined to present a problem only if it resulted in a blockage of the sample train. Silica gel is not recommended as a means of removing moisture, because it adsorbs significant amounts of the organic content. In the event that moisture removal should be required for some unforeseen circumstance, a condenser should be used to remove moisture and condensation.

SECTION 3

EXPERIMENTAL

The sampling train (Figures 1 and 2) consisted of a stainless steel probe connected to a Tedlar or mylar bag in a rigid leak-proof container. All connections were made with stainless steel or Teflon tubing with Swagelok connections. Swagelok connections were used rather than quick connects as specified in Method 23 in order to assure leak-free conditions. Bendix model BDX-44 personnel-monitoring pumps were pre-set and calibrated for the desired flow rate. These pumps, which were monitored by field staff, were used to pull the sample at a constant rate that was equalized between the pumps. The pumps had built-in flowmeters and control valves, which made them safe for operation in restricted areas that otherwise presented potential fire and explosion hazards. (See Appendix C for Method 23 analytical and sampling procedures.)

A leak-check procedure was developed that can be performed quickly in the field. The apparatus required for the procedure is shown in Figure 3. The leak-check procedure was as follows:

(a) Before the barrel container was sealed, the bag and its connection were visually inspected and the bag was evacuated with the sampling pump. Evacuation was continued until zero flow was detected, indicating that the bag and connection were leak-free. The bag inlet was then capped.

(b) Next, the container was sealed and checked for leaks by connecting the pump and gauge (Figure 3). The pump was turned on until the gauge indicated a vacuum of 1.2 kPa (5 in of water). The pinch clamp was then closed and the pump shut off. The time required for the vacuum to drop 0.25 kPa (1 in of water) was noted and compared to the allowable leakage rate shown in Figure 4. For instance, if a sampling rate of 1 l/min and a maximum allowable leakage of 10% is selected, the leak-check gauge should move no more than 0.19 kPa (0.75 in of water) in 1 min. During this procedure the drum is to be undisturbed and maintained at a constant temperature to avoid pressure changes from thermal expansion or contraction, or from pressure on the lid.

(c) The last step was a check of the probe and sample line connected to the bag. The pump and rotameter were connected to the end of the probe with a piece of tubing and checked for leaks. The end of the probe was plugged and the pump was kept running until zero flow was indicated.

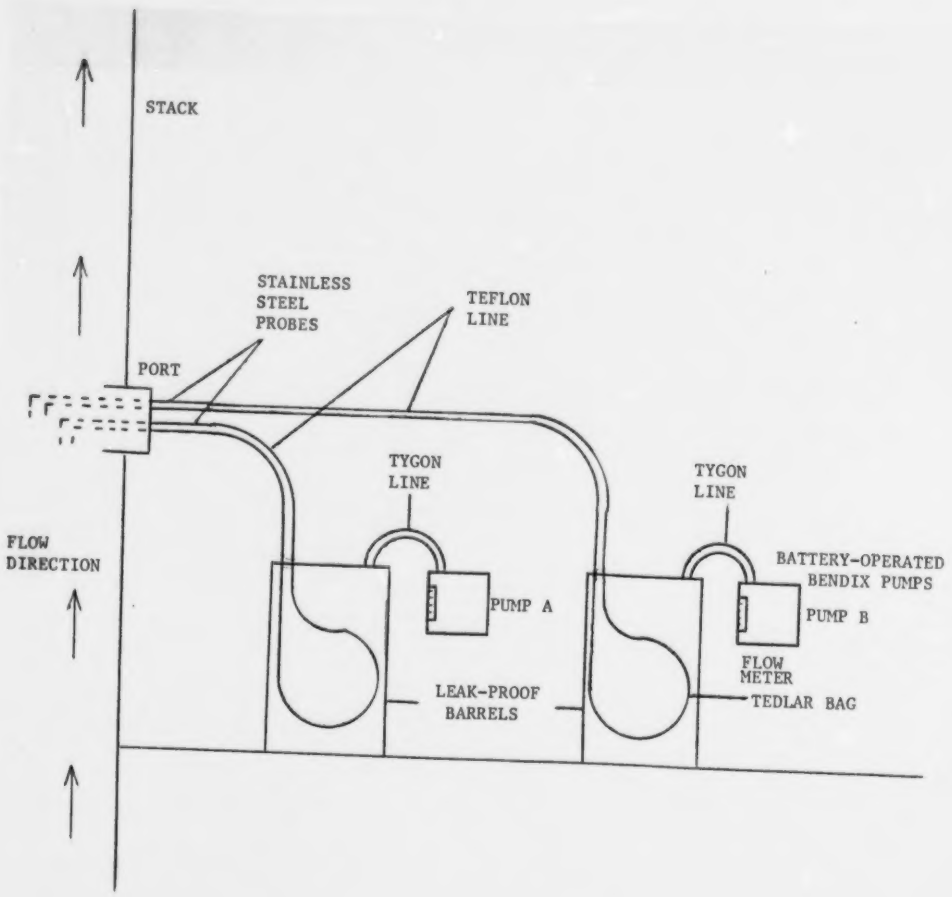


Figure 1. Sampling train on atmospheric vent.

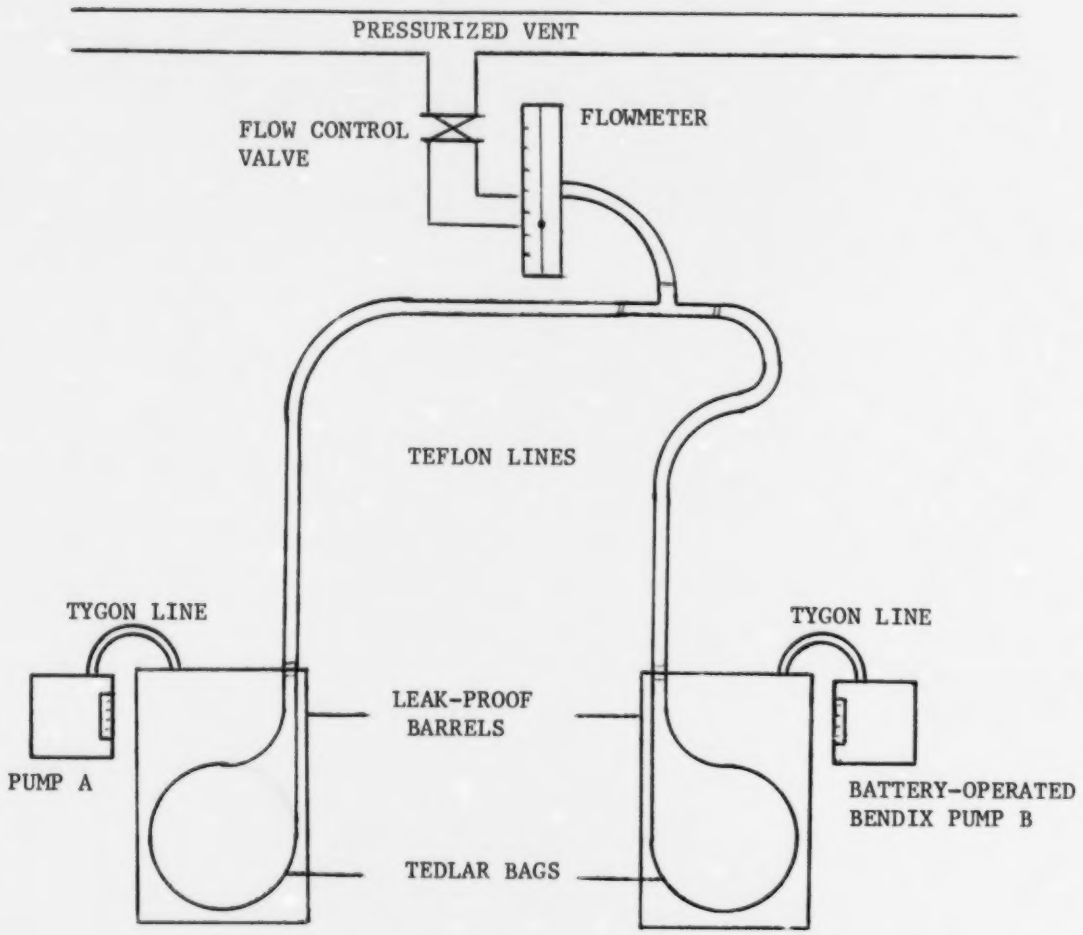


Figure 2. Sampling train on pressurized vent.

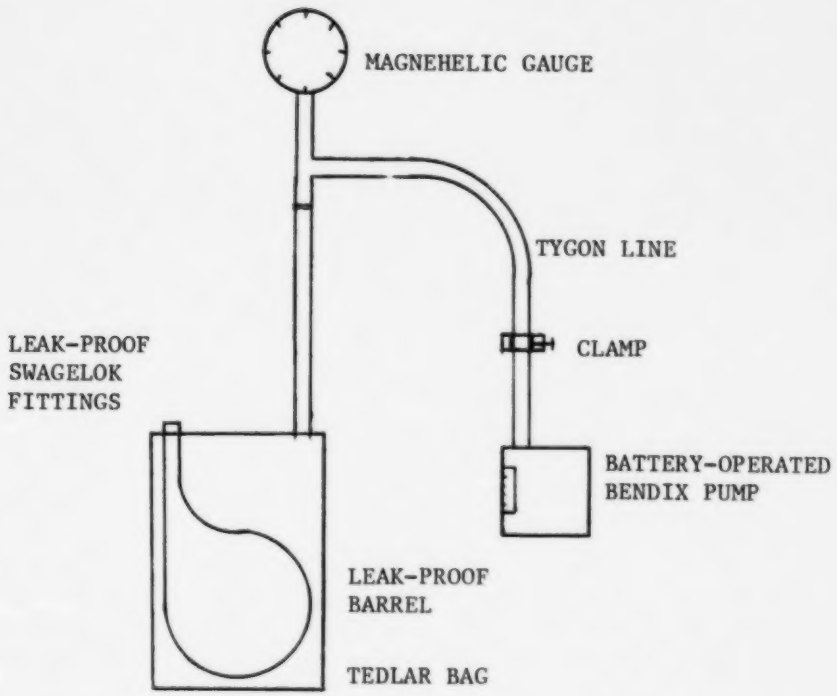


Figure 3. Leak-check apparatus.

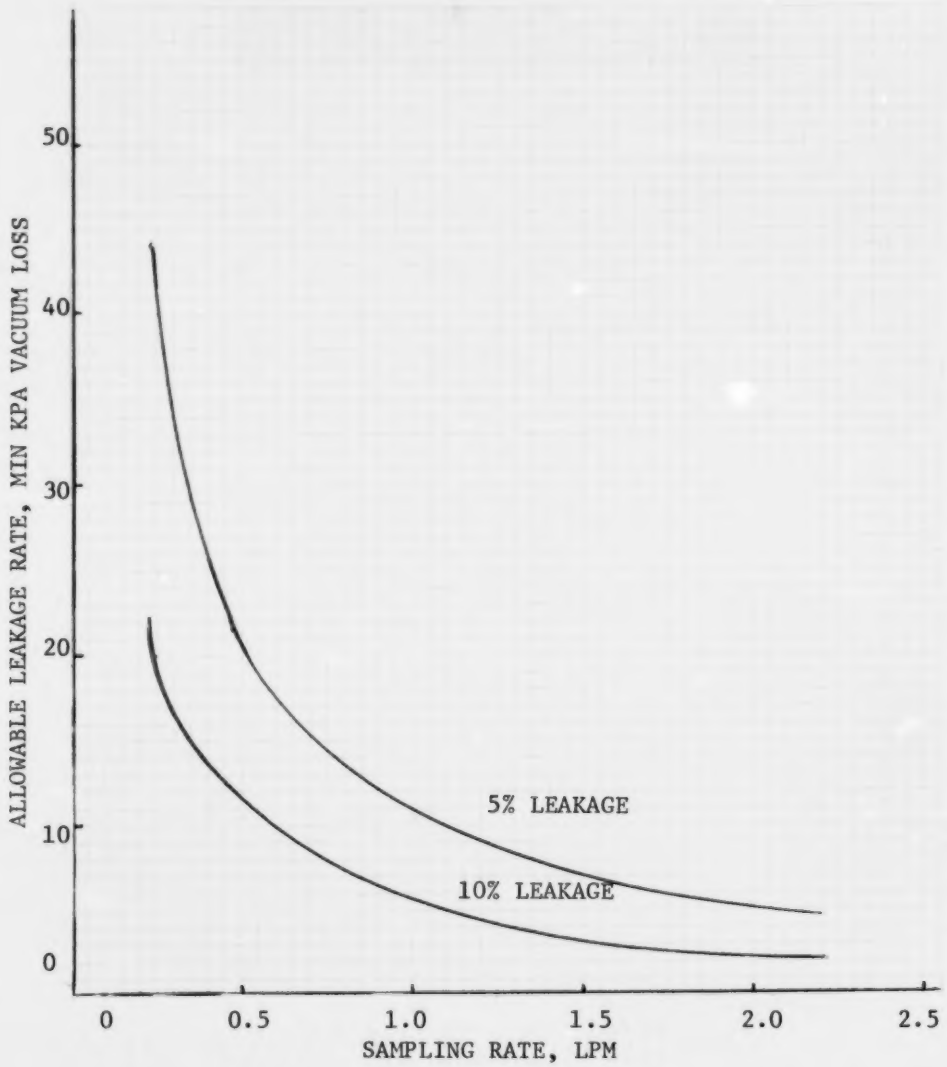


Figure 4. Allowable leakage rate per sampling rate. Calculated values for a 30-gal rigid container using an orifice flow equation.

The above procedure required extra time before the test, but was well worth while because it eliminated the problem of diluted samples or partially filled bags.

EVALUATION PARAMETERS

Sampling variables were chosen based on their likelihood of occurring under actual field conditions. Some choices were controllable variables, such as changes in the sampling rate or the type of bag used, whereas others were subject to chance, such as ambient temperature, sunlight exposure, or moisture condensation.

All gas samples were collected in pairs in identical sampling trains. One sampling train, A, was operated strictly by Method 23, i.e., protected from heat, shielded from sunlight during removal of the bag, sampled to achieve full volume, and analyzed within 30 to 60 min. The second sampling train, B, was varied in order to assess the effects of the parameters listed above.

At each site, both high and low concentrations were sampled. The variables and sample points for Train B are shown below (Table 1) for each compound sampled.

TABLE 1. METHOD 23 EVALUATION TEST VARIABLES, TRAIN B, TCE AND EDC

Test variables	Sample points				
	TCE			EDC	
	30 ppm	400 ppm	0.1 ppm*	20 ppm	2000 ppm
Duplicate samples	-	-	x	-	x
Sampling and storage temp.	x	x	-	x	x
Moisture condensation	-	-	x	-	-
Mylar bag**	x	x	-	x	x
Sample volume (1/2 vol.)	x	x	-	-	x
Exposure to light	x	x	-	-	x
Storage time	x	x	-	-	x

*Concentrations in this sample were below the detection limit of Method 23 (0.1 ppm) and, therefore, further evaluations were not carried out.

**All tests utilized Tedlar bags except when mylar was indicated.

Sampling and Storage Temperature

Depending on the season and the time of day, the temperature ranged from over 32°C (90°F) to less than 4°C (40°F). Two steel sampling drums were painted white and shaded from the sun for normal sampling. One drum was painted black and placed in the sum to maintain a higher sampling and storage temperature. Some samples were stored in a boiler room at more than 50°C (125°F) for 12 h.

Moisture Pretreatment

One of the sources to be tested (a thermal oxidizer with EDC feed) contained up to 60% moisture with a temperature as high as 82°C (180°F). Sample train A (control) allowed all moisture and condensation to enter the bag, whereas sample train B employed a condensing coil to remove moisture. Since this source contained nondetectable levels of EDC, no results could be obtained.

Bag type

The standard container was a 100-l Tedlar bag and the alternate was a 70-l aluminized mylar bag.

Sample Volume

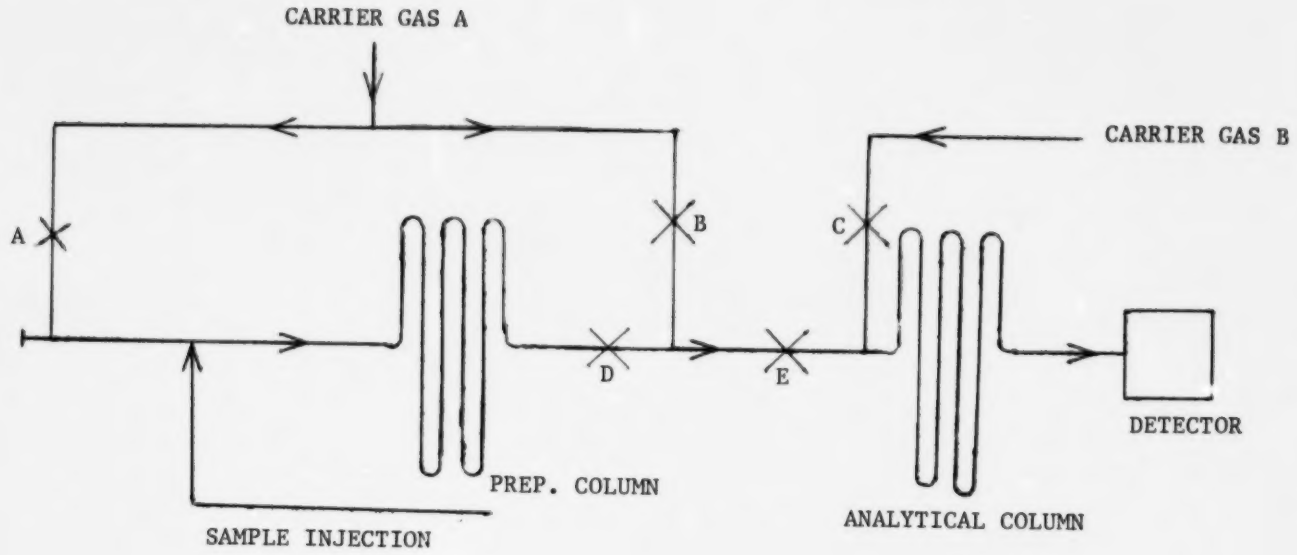
Sampling rates of 1.0 l/min for train A and 0.5 l/min for train B were used to evaluate the effect of a low sample volume. At the end of 1 to 1.5 h the sample volumes were 90 and 45-l respectively. Sampling at less than 0.5 l/min was not feasible with the pumps used for the experiment since they are designed to operate from 0.3 to 3 l/min.

Exposure to Light

Method 23 requires that the sample be protected from all natural light sources, particularly direct sunlight. In the second train, the bag was removed from the drum while exposed to the sun and was stored in the open, but out of direct sunlight. The bag was exposed to sunlight for approximately 5 min. Other previous samples were also exposed to sunlight and then reanalyzed to demonstrate the effect of this parameter. No controls or measurements of light intensity were incorporated; however, the intensity varied from a clear noon-hour sun to a slightly overcast day.

FIELD ANALYSIS

All gas samples collected were analyzed on site using a Shimadzu Mini 1 GC equipped with dual flame ionization detectors, dual electrometers, a heated sample loop, and a backflush system. Figure 5 shows a schematic of the GC column and backflush apparatus. The backflush system was composed of a ten-port sequence reversal valve and two columns, a scrubber column for retaining high molecular-weight compounds, and an analytical column. The sequence reversal valve reverses the carrier gas flow on the scrubber column



INJECT	BACKFLUSH
A, D, E OPEN	A, E CLOSED
B, C CLOSED	B, C, D OPEN

Figure 5. Gas chromatograph column configuration with backflush.

while maintaining constant flow on the analytical column. While the system was in the inject mode, the scrubber column and the analytical column were connected in series, allowing sample components to move through both columns. In the backflush mode the columns were disconnected from each other to become two separate systems, each with its own carrier gas source. This arrangement allowed for the separation and measurement of low molecular-weight compounds while the scrubber column was being backflushed of heavier sample components. Backflush times for different mixtures of sample components had to be predetermined to ensure that the compound(s) of interest were transferred to the analytical column before backflushing was started.

Samples for GC analysis were injected from the bag to a sample loop inlet through a short piece of Teflon tube connected in accordance with Method 23. The samples remained in the sample loop for 15 s to attain equilibrium, thus allowing the samples to reach atmospheric pressure and sample loop temperature before injection. Conditions used for the analysis were as follows:

Column (isothermal) temperature	100°C
Injector and detector temperature	200°C
5-ml sample loop temperature	50°C
Carrier gas flow rate	32 cm^3/min
Hydrogen flow rate	40 cm^3/min
Air flow rate	240 cm^3/min
Analysis time	5 min
Detector	Flame ionization

The columns used for field analysis were:

Scrubber column
  10% FFAP on Supelcoport 80/100
  3.2-mm x 1-m stainless steel
Analytical column
  20% SP-2100, 0.1% Carbowax 1500
  100/120 Supelcoport
  3.2-mm x 3.05-m stainless steel

QUALITY CONTROL

Preliminary to field testing, the accuracy of Method 23 was evaluated in three experiments. These experiments compared standard gas samples with the contents of samples taken previously from a certified cylinder standard or bag samples obtained earlier in the evaluation. The results are presented in the following table.

	Source concentration (ppm)	Sample concentration (ppm)	
		Train A	Train B
1)	19.64 (Tedlar bag)	16.1	16.2
2)	17.08 (Tedlar bag)	17.08	15.48 (mylar)
3)	9.4	9.34	-

These figures provided excellent preliminary validation necessary before field testing.

Laboratory standards, as listed below, were introduced into the GC before and during the analysis of samples. Replication of within 5% was first necessary before the analysis of field samples.

EDC (ppm)	TCE (ppm)
1024	49.6
51.7	9.18
9.66	

The values of field GC analysis of audit samples were compared with audit values, which were not disclosed until after the tests. The results were as follows:

TCE			EDC		
Audit value	Field analysis	Diff. (%)	Audit value	Field analysis	Diff. (%)
14.9	15.2	+2.0	9.2	9.75	+6.0
566	517	-8.7	438	448	+2.3

One of the audit cylinders was sampled with a Tedlar bag and the result was compared with the audit value to evaluate concentration losses from the sampling train. Results of this experiment were, in ppm, 9.2 for audit value, 9.75 for field analysis, 9.34 for the Tedlar bag, with a variation in the sample bag of +4.2%. New bags were provided for each sampling to avoid contamination from a previous sampling.

SECTION 4

RESULTS AND DISCUSSION

SAMPLING CONCENTRATIONS

This section discusses the results obtained during the testing program with respect to each of the variables presented in Section 3. A summary of all field data that were collected is presented in Appendix A.

Bag Type

The results of field evaluations using paired sampling trains revealed that the use of Tedlar bags as sampling containers resulted in concentration variations of less than 10% (ranging from 0.6% to 7.06%). Sampling with mylar bags, however, produced much larger variations. Samples collected in mylar bags yielded concentrations ranging from 9% to 43% lower than the concentrations measured from Tedlar bags. The results of these and other tests are presented in Tables 2 and 3 for TCE and EDC, respectively.

Heat, Volume, and Light

Analysis of the field data revealed that exposure to heat, reduced sample volume, and exposure to light had only minimal effects on measured sample concentrations. The differences in the analytical results due to these variations ranged from 1% to 7% when Tedlar bags were used. These differences ranged from 13% to 43% for samples collected in mylar bags. The results of these tests are presented in Tables 2 and 3.

TABLE 2. TCE FIELD EVALUATION RESULTS

Test no.*	Train A (ppm)	Train B (ppm)	Variations in train B	Percent variation
1	280	272	½ Volume/sunlight exposure	-2.8
2	345	195	½ Volume/mylar bag	-43.5
3	338	192	Heat/mylar bag	-43.2
4	369	373	Heat/sunlight exposure	+1.1
5	32	33	½ Volume	+3.1
6	34	20	Mylar bag	-41.2
7	43	40	Heat	-7.0
8	51	52	Sunlight exposure	+2.0

*Tedlar bags were used unless otherwise specified.

TABLE 3. EDC FIELD EVALUATION RESULTS

Test no.*	Train A (ppm)	Train B (ppm)	Variations in train B	Percent variation
**	1816	1821	None	+0.3
5	1764	1699	Heat/½ volume	-3.7
6	1796	1459	Mylar/½ volume	-18.8
7	1764	1538	Heat/mylar bag	-12.8
9	16.1	16.1	Heat	+0.6
10	17.08	15.48	Mylar bag	-9.4

*Tedlar bags were used unless otherwise specified.
**Tests No. 1-3 contained nondetectable levels of EDC.

MOISTURE PRETREATMENT

The effects of condensing moisture in the sampling train could not be demonstrated since the only source containing moisture contained nondetectable levels of EDC. However, preparatory work in the laboratory showed that silica gel adsorbed various organics including TCE and EDC and was, therefore, not suitable for preconditioning the sample. Figure 6 depicts the outlet of a silica gel tube compared to its inlet volume for three organics. As shown on this figure, over 90% of a sample volume of 30 l of EDC was adsorbed.

In other laboratory experiments, distilled water was added to samples of TCE and EDC in Tedlar bags, and no effect on the concentration was evident. Thus, precondensing moisture seemed unnecessary except where moisture content was so great that sampling could have been impeded. During the field tests, the probe and the sampling line were arranged to slope downhill from the sample port to the bag to prevent blockage from accumulated water droplets.

STORAGE TIME

The results of the analysis of sample degradation over time are presented in Table 4. These data indicate that samples degrade approximately twice as rapidly in mylar bags as in Tedlar bags. Regression analysis of the data indicate that TCE samples held in Tedlar bags degrade at an average rate of approximately 1% per day whereas samples in mylar bags degrade at a rate of 2% per day.

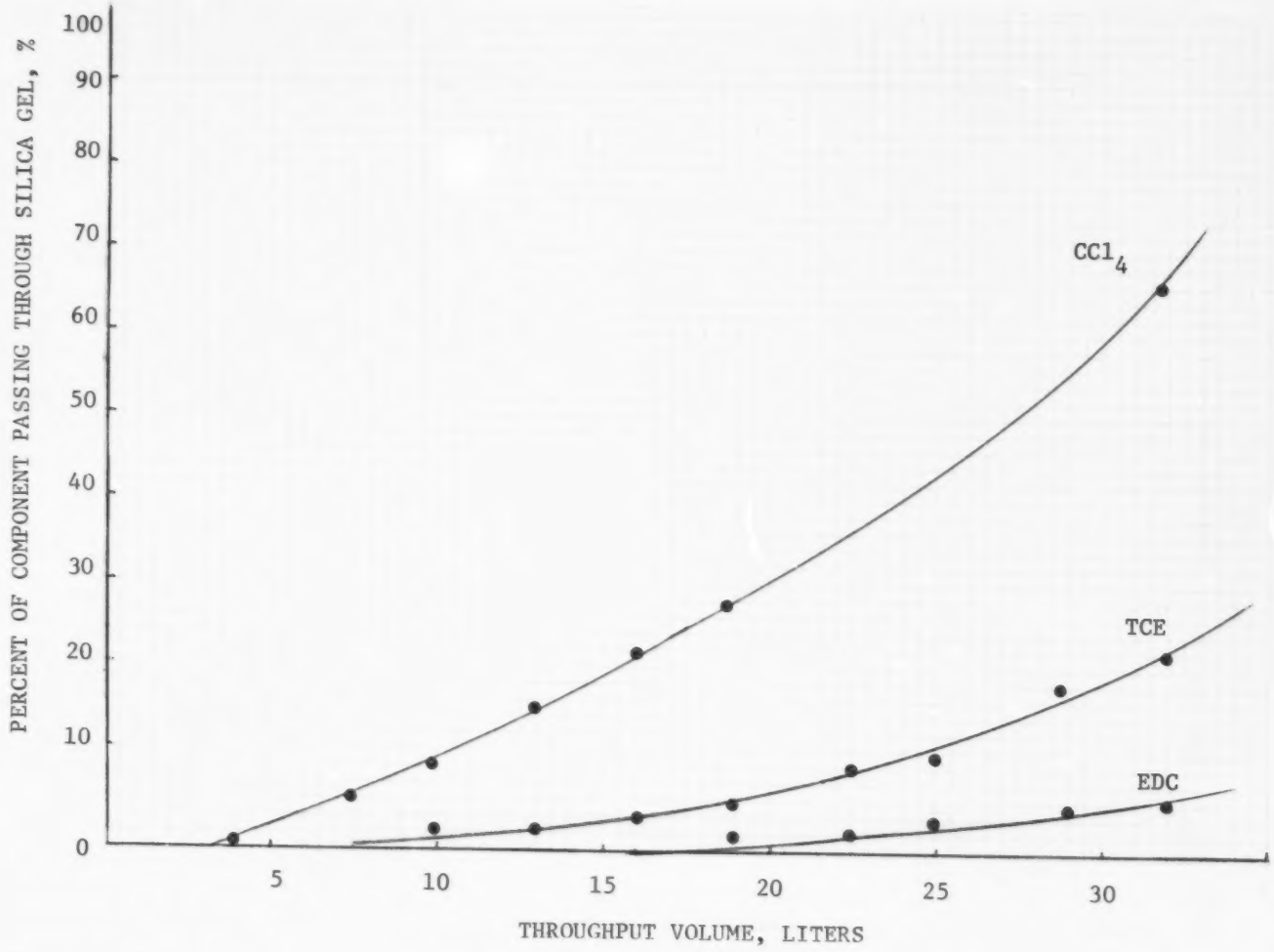


Figure 6. Adsorption profile of silica gel with EDC, TCE, and CCl_4.

TABLE 4. SAMPLE DEGRADATION OVER TIME

Test no.	Sample train	Bag type	Concentration, ppm TCE Days after sampling 0	1	5	7	9
1	A	T	280	275	-	-	-
	B	T	272	268	-	-	-
2	A	T	345	342	-	-	-
	B	M	195	168	-	-	157
3	A	T	338	314	-	-	280
	B	M	192	186	-	-	152
4	A	T	369	353	-	-	-
	B	T	373	345	-	-	-
5	A	T	32	33	-	36	-
	B	T	33	31	-	30	-
6	A	T	34	30	-	26	-
	B	M	20	20	-	16	-
7	A	T	43	-	-	-	-
	B	T	40	-	-	-	-
8	A	T	51	-	46	-	-
	B	T	52	-	49	-	-

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APPENDIX A

FIELD DATA SUMMARY

TABLE A-1. FIELD DATA SUMMARY - METHOD 23 FIELD EVALUATION, TCE

Sample		Bag type	Sample rate	Sample time	Variations	Concentration
Test no.	Train A/B	T/M	(lpm)	(min)	Heat, sunlight	(ppm)
1	A	T	1.2	65	-	280
	B	T	0.6	65	3 min. sunlight	272
2	A	T	1.3	75	-	345
	B	M	0.64	75	-	195
3	A	T	0.48	140	-	338
	B	M	0.48	140	Overnight heat	192
4	A	T	0.5	120	-	369
	B	T	0.48	120	Sunlight, heat	373
5	A	T	1.5	90	-	32
	B	T	0.7	90	-	33
6	A	T	0.79	135	-	34
	B	M	0.85	135	-	20
7	A	T	1.2	81	-	43
	B	M	1.2	81	Heat	40
8	A	T	1.2	85	-	51
	B	T	1.2	85	4 min. sunlight	52

TABLE A-2. FIELD DATA SUMMARY - METHOD 23 FIELD EVALUATION, EDC

Sample		Bag type	Sample rate	Sample time	Variations	Concentration
Test no.	Train A/B	T/M	(lpm)	(min)	Heat, sunlight	(ppm)
1	A	T	1.89	40	-	None detected*
	B	T	1.85	40	Heat	None detected
2	A	T	2.27	45	-	None detected
	B	T	2.21	45	Condenser	None detected
4	A	T	2.21	30	-	1816
	B	T	2.27	30	-	1821
5	A	T	2.02	35	-	1764 (1731 sunlight)
	B	T	0.66	35	Heat	1699
6	A	T	2.02	55	-	1796
	B	M	0.66	55	-	1459
7	A	T	1.26	55	-	1764
	B	M	1.08	55	Heat	1538
9	A	T	1.7	47	-	16.1
	B	T	1.5	47	Heat	16.2
10	A	T	1.5	45	-	17.08
	B	M	1.5	45	-	15.48
11	A	T	0.75	45	Audit cylinder	9.34

*Detection limit estimated to be 0.1 ppm.

APPENDIX B

FIELD AUDIT REPORT

FIELD AUDIT REPORT

PART A - To be filled out by organization supply unit cylinders (RTI)

1. Organization supplying audit sample(s) and shipping address

   Research Triangle Institute, P.O. Box 12194, Research Triangle Park, NC 27711

2. Audit supervisor, organization, and phone number (EMB Technical Manager)

   Joe Knoll, EPA

3. Shipping instructions - Name, Address, Attention

   Byron Bradd; Scott Environmental Technology

   Post Office Box D-11

   Plumsteadville, PA 18949

4. Guaranteed arrival date for cylinders 9/18/80

5. Planned shipping date for cylinders 9/11/80

6. Details on audit cylinders for last analysis

		Low Conc.	High Conc.
a.	Date of last analysis	8/6/80	8/24/79
b.	Cylinder number	BAL 427	BAL 400
c.	Cylinder pressure, PSI	1500	1500
d.	Audit gas(es)/balance gas	Trichloroethylene/N_2	Trichloroethylene/N_2
e.	Audit gas(es) ppm	~~566~~ 14.9	566
f.	Cylinder construction	Aluminum	Aluminum

PART B - To be filled out by audit supervisor

1. Organic chemical manufacturing process Degreasing Unit

2. Location of audit Warminster, PA

3. Name of individual audit and organization Ryan Bradley
Scott Environmental Technology

4. Audit results

		Low Conc.	High Conc.
a.	Cylinder number		
b.	Cylinder pressure before audit, psi		
c.	Cylinder pressure after audit, psi		
d.	Audit date and measured concentration, ppm		
	Date		
	Analysis #1 9/16/80	15.17	.517
	Analysis #2 9/16/80	14.51	.517
	Analysis #3		
e.	RTI concentration, ppm (Part A, 6d)	14.9	566

f. Audit accuracy*

Analysis #1	+ 1.8	- 8.7
Analysis #2	- 2.6	
Analysis #3		

*Percent accuracy = $\frac{\text{Measured Conc. - RTI Conc.}}{\text{RTI Conc.}} \times 100$

g. Problems detected (if any) None.

APPENDIX C

METHOD FOR THE DETERMINATION OF HALOGENATED ORGANICS FROM STATIONARY SOURCES

METHOD 23. DETERMINATION OF HALOGENATED ORGANICS FROM STATIONARY SOURCES

INTRODUCTION

Performance of this method should not be attempted by persons unfamiliar with the operation of a gas chromatograph, nor by those who are unfamiliar with source sampling, as there are many details that are beyond the scope of this presentation. Care must be exercised to prevent exposure of sampling personnel to hazardous emissions.

1. Principle and Applicability

1.1 Principle. An integrated bag sample of stack gas containing one or more halogenated organics is subjected to gas chromatographic (GC) analysis, using a flame ionization detector (FID).

1.2 Applicability. The method is applicable to the measurement of halogenated organics such as carbon tetrachloride, ethylene dichloride, perchloroethylene, trichloroethylene, methylene chloride, 1-1-1 trichloroethane, and trichlorotrifluoroethane in stack gases only from specified processes. It is not applicable where the gases are contained in particulate matter.

2. Range and Sensitivity

The procedure described herein is applicable to the measurement of halogenated organics in the 0.1 to 200 ppm range. The upper limit may be extended by further calibration or by dilution of the sample.

3. Interferences

The chromatograph column with the corresponding operating parameters herein described has been represented as being useful for producing adequate resolution of halogenated organics. However, resolution

interferences may be encountered on some sources. Also, the chromatograph operator may know of a column that will produce a superior resolution of the particular compound of interest without reducing the response to that compound, as specified in Section 4.3.1.

In any event, the chromatograph operator shall select a column which is best suited to his particular analysis problem, subject to the approval of the Administrator. Such approval shall be considered automatic provided that confirming data produced through a demonstrably adequate supplemental analytical technique, such as analysis with a different column or G.C./mass spectroscopy, is available for review by the Administrator.

4. Apparatus

4.1 Sampling (see Figure 23-1).

4.1.1 Probe. Stainless steel, Pyrex[1] glass, or Teflon tubing according to stack temperature, each equipped with a glass wool plug to remove particulate matter if particulate matter is present.

4.1.2 Sample Line. Teflon, 6.4 mm outside diameter, of sufficient length to connect probe to bag. A new unused piece is employed for each series of bag samples that constitutes an emission test.

4.1.3 Male (2) and female (2) stainless steel quick connects, with ball checks (one pair without) located as shown in Figure 23-1.

4.1.4 Tedlar or aluminized Mylar bags, 100 liter capacity. To contain sample.

4.1.5 Rigid leakproof containers for 4.1.4, with covering to protect contents from sunlight.

[1] Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.

4.1.6 Needle Valve. To adjust sample flow rate.

4.1.7 Pump--Leak-Free. Minimum capacity 2 liters per minute.

4.1.8 Charcoal Tube. To prevent admission of halogenated organics to the atmosphere in the vicinity of samplers.

4.1.9 Flow Meter. For observing sample flow rate; capable of measuring a flow range from 0.10 to 1.00 liters per minute.

4.1.10 Connecting Tubing. Teflon, 6.4 mm outside diameter, to assemble sample train (Figure 23-1).

4.2 Sample Recovery.

4.2.1 Tubing. Teflon, 6.4 mm outside diameter, to connect bag to gas chromatograph sample loop. A new unused piece is employed for each series of bag samples that constitutes an emission test, and is to be discarded upon conclusion of analysis of those bags.

4.3 Analysis.

4.3.1 Gas Chromatograph. With FID, potentiometric strip chart recorder and 1.0 to 2.0 ml sampling loop in automatic sample valve. The chromatographic system shall be capable of producing a response to 0.1 ppm of the halogenated organic compound that is at least as great as the average noise level. (Response is measured from the average value of the baseline to the maximum of the waveform, while standard operating conditions are in use.)

4.3.2 Chromatographic Column. Stainless steel, 3.05 m x 3.2 mm, containing 20 percent SP-2100/0.1 percent Carbowax 1500 on 100/120 Supelcoport. Other columns can be used, provided that the precision and accuracy of the analysis of standards are not impaired. Information confirming that adequate resolution of the halogenated organic compound

peak is accomplished should be available. Adequate resolution is defined as an area overlap of not more than 10 percent of the halogenated organic compound peak by an interferent peak. Calculation of area overlap is explained in Appendix E, Supplement A: "Determination of Adequate Chromotographic Peak Resolution."

4.3.3 Flow Meters (2). Rotameter type, 0 to 100 ml/min capacity.

4.3.4 Gas Regulators. For required gas cylinders.

4.3.5 Thermometer. Accurate to one degree centigrade, to measure temperature of heated sample loop at time of sample injection.

4.3.6 Barometer. Accurate to 5 mm Hg, to measure atmospheric pressure around gas chromatograph during sample analysis.

4.3.7 Pump--Leak-free. Minimum capacity 100 ml/min.

4.3.8 Recorder. Strip chart type, optionally equipped with disc integrator or electronic integrator.

4.3.9 Planimeter. Optional, in place of disc or electronic integrator, for 4.3.8 to measure chromatograph peak areas.

4.4 Calibration. 4.4.2 through 4.4.6 are for section 7.1 which is optional.

4.4.1 Tubing. Teflon, 6.4 mm outside diameter, separate pieces marked for each calibration concentration.

4.4.2 Tedlar or Aluminized Mylar Bags. 50-liter capacity, with valve; separate bag marked for each calibration concentration.

4.4.3 Syringe. 25 µl, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.4 Syringe. 50 µl, gas tight, individually calibrated, to dispense liquid halogenated organic solvent.

4.4.5 Dry Gas Meter, With Temperature and Pressure Gauges. Accurate to ±2 percent, to meter nitrogen in preparation of standard gas mixtures, calibrated at the flowrate used to prepare standards.

4.4.6 Midget Impinger/Hot Plate Assembly. To vaporize solvent.

5. Reagents

It is necessary that all reagents be of chromatographic grade.

5.1 Analysis.

5.1.1 Helium Gas or Nitrogen Gas. Zero grade, for chromatographic carrier gas.

5.1.2 Hydrogen Gas. Zero grade.

5.1.3 Oxygen Gas or Air as Required by the Detector. Zero grade.

5.2 Calibration. Use one of the following options: either 5.2.1 and 5.2.2, or 5.2.3.

5.2.1 Halogenated organic compound, 99 mol percent pure, certified by the manufacturer to contain a minimum of 99 mol percent of the particular halogenated organic compound; for use in the preparation of standard gas mixtures as described in Section 7.1.

5.2.2 Nitrogen Gas. Zero grade, for preparation of standard gas mixtures as described in Section 7.1.

5.2.3 Cylinder Standards (3). Gas mixture standards (200, 100, and 50 ppm of the halogenated organic compound of interest, in nitrogen) for which the gas composition has been certified with an accuracy of ±3 percent or better by the manufacturer. The manufacturer must have recommended a maximum shelf life for each cylinder so that the concentration

does not change by greater than ± 5 percent from the certified value. The date of gas cylinder preparation, certified concentration of the halogenated organic compound and recommended maximum shelf life must have been affixed to the cylinder before shipment from the gas manufacturer to the buyer. These gas mixture standards may be directly used to prepare a chromatograph calibration curve as described in Section 7.2.2.

5.2.3.1 Cylinder Standards Certification. The concentration of the halogenated organic compound in nitrogen in each cylinder must have been certified by the manufacturer by a direct analysis of each cylinder using an analytical procedure that the manufacturer had calibrated on the day of cylinder analysis. The calibration of the analytical procedure shall, as a minimum, have utilized a three-point calibration curve. It is recommended that the manufacturer maintain two calibration standards and use these standards in the following way: (1) a high concentration standard (between 200 and 400 ppm) for preparation of a calibration curve by an appropriate dilution technique; (2) a low concentration standard (between 50 and 100 ppm) for verification of the dilution technique used. If the difference between the apparent concentration read from the calibration curve and the true concentration assigned to the low concentration standard exceeds 5 percent of the true concentration, determine the source of error and correct it, then repeat the three-point calibration.

5.2.3.2 Establishment and Verification of Calibration Standards. The concentration of each calibration standard must have been established by the manufacturer using reliable procedures. Additionally, each calibration standard must have been verified by the manufacturer by

one of the following procedures, and the agreement between the initially determined concentration value and the verification concentration value must be within ± 5 percent: (1) verification value determined by comparison with a gas mixture prepared in accordance with the procedure described in Section 7.1.1 and using 99 mol percent of the halogenated organic compounds, or (2) verification value obtained by having the calibration standard analyzed by the National Bureau of Standards, if such analysis is available. All calibration standards must be reverified on a time interval consistent with the shelf life of the cylinder standards sold.

5.2.4 Audit Cylinder Standards (2). Gas mixture standards identical in preparation to those in Section 5.2.3 (the halogenated organic compounds of interest, in nitrogen), except the concentrations are only known to the person supervising the analysis of samples. The concentrations of the audit cylinders should be: one low concentration cylinder in the range of 25 to 50 ppm, and one high concentration cylinder in the range of 200 to 300 ppm. When available, audit cylinders may be obtained by contacting: EPA, Environmental Monitoring and Support Laboratory, Quality Assurance Branch (MD-77), Research Triangle Park, North Carolina 27711. If audit cylinders are not available at EPA, an alternate source must be secured.

6. Procedure

6.1 Sampling. Assemble the sample train as in Figure 23-1. Perform a bag leak check according to Section 7.3.2. Join the quick connects as illustrated, and determine that all connections between the bag and the probe are tight. Place the end of the probe at the

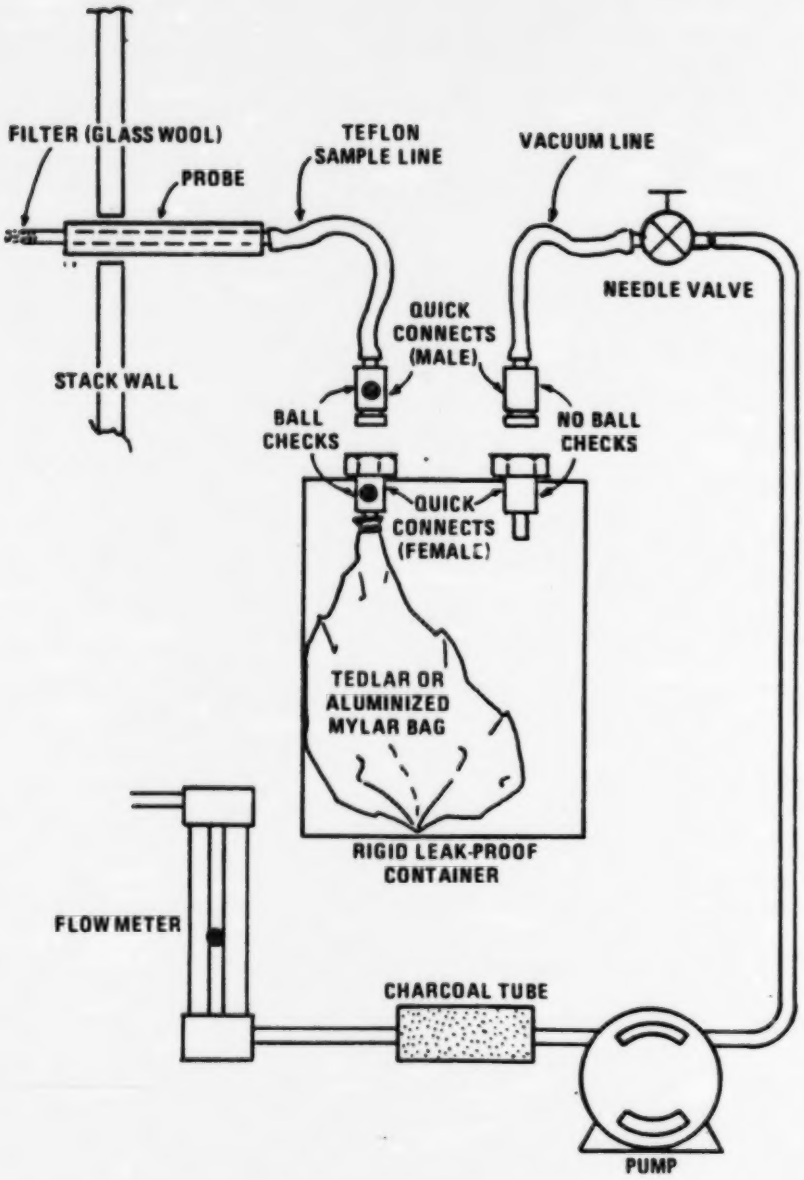

Figure 23-1. Integrated bag sampling train

centroid of the stack and start the pump with the needle valve adjusted to yield a flow of 0.5 lpm. After a period of time sufficient to purge the line several times has elapsed, connect the vacuum line to the bag and evacuate the bag until the rotameter indicates no flow. At all times, direct the gas exiting the rotameter away from sampling personnel. Then reposition the sample and vacuum lines and begin the actual sampling, keeping the rate constant. At the end of the sample period, shut off the pump, disconnect the sample line from the bag, and disconnect the vacuum line from the bag container. Protect the bag container from sunlight.

6.2 Sample Storage. Sample bags must be kept out of direct sunlight and must be protected from heat. Analysis must be performed within 1 day of sample collection for methylene chloride, ethylene dichloride and trichlorotrifluoroethane. Analysis of perchloroethylene, trichloroehtylene, 1, 1, 1-trichloroethane and carbon tetrachloride must be performed within 2 days.

6.3 Sample Recovery. With a new piece of Teflon tubing identified for that bag, connect a bag inlet valve to the gas chromatograph sample valve. Switch the valve to receive gas from the bag through the sample loop. Arrange the equipment so the sample gas passes from the sample valve to a 0-100 ml/min rotameter with flow control valve followed by a charcoal tube and a 0-1 inch w.g. pressure gauge. Sample flow may be maintained either by a vacuum pump or container pressurization if the collection bag remains in the rigid container. After sample loop purging is ceased, allow the pressure gauge to return to zero before activating the gas sampling valve.

6.4 Analysis. Set the column temperature to 100° C, and the detector temperature to 225° C. When optimum hydrogen and oxygen flow rates have been determined, verify and maintain these flow rates during all chromatograph operations. Using zero helium or nitrogen as the carrier gas, establish a flow rate in the range consistent with the manufacturer's requirements for satisfactory detector operation. A flow rate of approximately 20 ml/min should produce adequate separations. Observe the base line periodically and determine that the noise level has stabilized and that base line drift has ceased. Purge the sample loop for thirty seconds at the rate of 100 ml/min, then activate the sample valve. Record the injection time (the position of the pen on the chart at the time of sample injection), the sample number, the sample loop temperature, the column temperature, carrier gas flow rate, chart speed and the attenuator setting. Record the laboratory pressure. From the chart, note the peak having the retention time corresponding to the halogenated organic compound as determined in Section 7.2.1. Measure the halogenated organic compound peak area, A_m, by use of a disc integrator, electronic integrator, or a planimeter. Record A_m and the retention time. Repeat the injection at least two times or until two consecutive values for the total area of the peak do not vary more than 5 percent. The average value for these two total areas will be used to compute the bag concentration.

6.5 Measure the ambient temperature and barometric pressure near the bag. From a water saturation vapor pressure table, determine and record the water vapor content of the bag as a decimal figure. (Assume the relative humidity to be 100 percent unless a lesser value is known.)

7. Standards, Calibration, and Quality Assurance

7.1 Standards.

7.1.1 Preparation of Standard Gas Mixtures. (Optional-delete if cylinder standards are used.) Assemble the apparatus shown in Figure 23-2. Check that all fittings are tight. Evacuate a 50-liter Tedlar or aluminized Mylar bag that has passed a leak check (described in Section 7.3.2) and meter in about 50 liters of nitrogen. Measure the barometric pressure, the relative pressure at the dry gas meter, and the temperature at the dry gas meter. Refer to Table 23-1. While the bag is filling, use the 50 μl syringe to inject through the septum on top of the impinger, the quantity required to yield a concentration of 200 ppm. In a like manner, use the 25 μl syringe to prepare bags having approximately 100 and 50 ppm concentrations. To calculate the specific concentrations, refer to Section 8.1. Tedlar bag gas mixture standards of methylene chloride, ethylene dichloride, and trichlorotrifluoroethane may be used for 1 day; trichloroethylene and 1, 1,1-trichloroethene for 2 days; perchloroethylene and carbon tetrachloride for 10 days from the date of preparation. (Caution: Contamination may be a problem when a bag is reused if the new gas mixture standard is a lower concentration than the previous gas mixture standard.)

7.2 Calibration.

7.2.1 Determination of Halogenated Organic Compound Retention Time. This section can be performed simultaneously with Section 7.2.2. Establish chromatograph conditions identical with those in Section 6.3, above. Determine proper attenuator position. Flush the sampling loop with zero helium or nitrogen and activate the sample valve. Record the

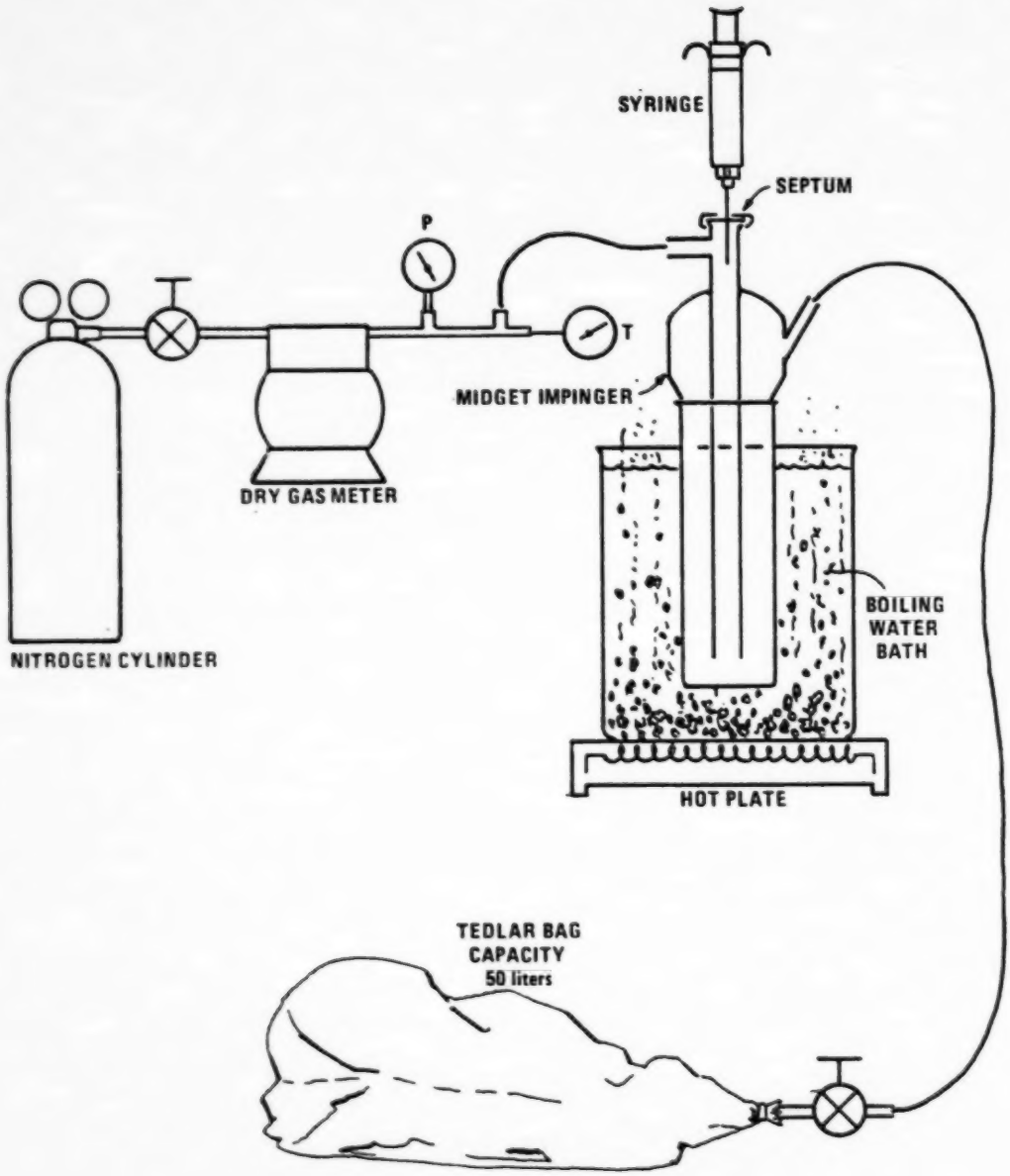

Figure 23-2. Train for preparation of samples

TABLE 23-1. INJECTION VALUES FOR PREPARATION OF STANDARDS. (Optional, see Section 7.1.1)

Compound	Molecular Weight (M)	Density at 293° A (D)	µl Liquid Required in 50 l N_2 for Approximate Concentration of:		
			200 ppm	100 ppm	50 ppm
Perchloroethylene C_2Cl_4	165.85	1.6230	42.5	21.2	10.6
Trichloroethylene C_2HCl_3	131.40	1.4649	37.3	18.6	9.3
1,1,1-Trichloroethane $C_2H_3Cl_3$	133.42	1.4384	38.6	19.3	9.6
Methylene Chloride CH_2Cl_2	84.94	1.3255	26.6	13.3	6.7
Trichlorotrifluoroethane $C_2Cl_3F_3$	187.38	1.5790	49.3	24.7	12.3
Carbon Tetrachloride CCl_4	153.84	1.5940	40.1	20.1	10.0
Ethylene Dichloride $C_2H_4Cl_2$	98.96	1.2569	32.7	16.4	8.2

injection time, the sample loop temperature, the column temperature, the carrier gas flow rate, the chart speed and the attenuator setting. Record peaks and detector responses that occur in the absence of the halogenated organic. Maintain conditions (with the equipment plumbing arranged identically to Section 6.3), flush the sample loop for 30 seconds at the rate of 100 ml/min with one of the halogenated organic compound calibration mixtures, and activate the sample valve. Record the injection time. Select the peak that corresponds to the halogenated organic compound. Measure the distance on the chart from the injection time to the time at which the peak maximum occurs. This distance divided by the chart speed is defined as the halogenated organic compound peak retention time. Since it is possible that there will be other organics present in the sample, it is very important that positive identification of the halogenated organic compound peak be made.

7.2.2 Preparation of Chromatograph Calibration Curve. Make a gas chromatographic measurement of each standard gas mixture (described in Section 5.2.3 or 7.1.1) using conditions identical with those listed in Sections 6.3 and 6.4. Flush the sampling loop for 30 seconds at the rate of 100 ml/min with one of the standard gas mixtures and activate the sample valve. Record C_c, the concentration of halogenated organic injected, the attenuator setting, chart speed, peak area, sample loop temperature, column temperature, carrier gas flow rate, and retention time. Record the laboratory pressure. Calculate A_c, the peak area multiplied by the attenuator setting. Repeat until two consecutive injection areas are within 5 percent, then plot the average of those two

values versus C_c. When ther other standard gas mixtures have been similarly analyzed and plotted, draw a straight line through the points. Perform calibration daily, or before and after each set of bag samples, whichever is more frequent.

7.3 Quality Assurance.

7.3.1 Analysis Audit. Immediately after the preparation of the calibration curve and prior to the sample analyses, perform the analysis audit described in Appendix E, Supplement B: "Procedure for Field Auditing GC Analysis."

7.3.2 Bag Leak Checks. While performance of this section is required subsequent to bag use, it is also advised that it be performed prior to bag use. After each use, make sure a bag did not develop leaks as follows: to leak check, connect a water manometer and pressurize the bag to 5-10 cm H_2O (2-4 in. H_2O). Allow to stand for 10 minutes. Any displacement in the water manometer indicates a leak. Also, check the rigid container for leaks in this manner. (Note: an alternative leak check method is to pressurize the bag to 5-10 cm H_2O or 2-4 in. H_2O and allow to stand overnight. A deflated bag indicates a leak.) For each sample bag in its rigid container, place a rotameter in line between the bag and the pump inlet. Evacuate the bag. Failure of the rotameter to register zero flow when the bag appears to be empty indicates a leak.

8. Calculations

8.1 Optional Standards Concentrations. Calculate each halogenated organic standard concentration prepared in accordance with Section 7.1.1 as follows:

$$C_c = \frac{B\mu l \ \frac{D\ \mu g}{\mu l} \ \frac{10^3\ \mu g}{mg} \ \frac{\mu g\ mole}{M\ \mu g} \ \frac{24.055\ \mu l}{\mu g\ mole} \ 10^6}{V_m\ Y\ \frac{10^6\ \mu l}{l} \ \frac{293}{T_m} \ \frac{P_m}{760}}$$

$$= \frac{\frac{BD}{M}\ (24.055 \times 10^3)}{V_m\ Y\ \frac{293}{T_m}\ \frac{P_m}{760}} \qquad \text{Equation 23-1}$$

Where:

C_c = Standard concentration in ppm.

B = Number of µl of injected.

V_m = Gas volume measured by dry gas meter in liters.

Y = Dry gas meter calibration factor.

P_m = Absolute pressure of the dry gas meter, mm Hg.

T_m = Absolute temperature of the dry gas meter, °A.

D = Density of compound at 293° A.

M = Molecular weight of compound.

24.055= Ideal gas at 293° A, 760 mm Hg.

10^6 = Conversion factor, ppm.

8.2 Sample Concentrations. From the calibration curve described in Section 7.2.2 above, select the value of C_c that corresponds to A_c. Calculate C_s as follows:

$$C_s = \frac{C_c P_r T_i}{P_i T_r\ (1-S_{wb})} \qquad \text{Equation 23-2}$$

Where:

S_{wb} = The water vapor content of the bag sample, as analyzed.

C_s = The concentration of the halogenated organic in the sample in ppm.

C_c = The concentration of the halogenated organic indicated by the gas chromatograph, in ppm.

P_r = The reference pressure, the laboratory pressure recorded during calibration, mm Hg.

T_i = The sample loop temperature on the absolute scale at the time of analysis, °A.

P_i = The laboratory pressure at time of analysis, mm Hg.

T_r = The reference temperature, the sample loop temperature recorded during calibration, °A.

9. References

1. Feairheller, W. R.; Kemmer, A.M.; Warner, B. J.; and Douglas, D. Q. "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," EPA Contract No. 68-02-1404, Task 33 and 68-02-2818, Work Assignment 3. January 1978. Revised August, 1978, by EPA.

2. Bullein 747. "Separation of Hydrocarbons" 1974. Supelco, Inc. Bellefonte, Pennsylvania 16823.

3. Communication From Joseph E. Knoll. Perchloroethylene Analysis by Gas Chromatography. March 8, 1978.

4. Communication From Joseph E. Knoll. Test Method for Halogenated Hydrocarbons. December 20, 1978.